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By:  Date: December 7, 2004

Docket No.: 9913/9-1802

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: Johan C. FITTER Conf. 9478
Serial No.: 09/739,483 Group Art Unit: 1745
Filing Date: December 18, 2000 Examiner: G. Cantelmo
For: AN ELECTROCHEMICAL CELL

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

DECLARATION UNDER 37 CFR 1.132

Sir:

1. I, Johan C. Fitter, am the sole inventor of the subject matter claimed in the above referenced application.
2. I have reviewed the office action dated August 9, 2004, as well as the translated portions of JP 10-302785A, and JP50-091728.
3. My invention is directed to a rechargeable electrochemical cell which is subjected to multiple charging and discharging cycles, each charging cycle having a charging portion corresponding to a gassing charge where gas is generated and a charging portion below the gassing charge. I have found that the presence of charge dependant impeding means, now more properly termed "deactivatable impeding means", disposed in the electrolyte and having a

¹
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constituent bonded to the negative electrodes of the electrochemical cell forms an "on/off" barrier for impeding the gassing charge. The term "deactivatable" is defined in my claims as meaning that the impeding means are activated by the charging portion corresponding to the gassing charge ("turned on") and are deactivated ("turned off") when the charging portion falls below the gassing charge to limit gas generation, and additionally, when turned off, have no charge limiting effect below the gassing charge, and substantially no effect during the discharge cycle.

2. That these means are therefore "deactivatable impeding means" is of particular importance, and this is related to the structural arrangement between the means and the electrode.

With the correct attachment, charging and discharging proceed normally, activation of the impeding effect only occurring when the gassing charge level is reached, as described in the patent specification, pg. 21 line 21 to pg. 22, line 2, with reference to Figures 4 and 5. The ability of the means to be "deactivatable", that is, turned on or off depending on the charge, is believed related to the specific type of attachment or bonding of the means to the negative electrode.

3. For example, as shown in Figure 6, the means comprise quaternary ammonium compounds 38 with "heads" attached to the electrode surface, and "tails" extending into the electrolyte, thereby impeding ion transport, and so the orientation is believed to be necessary to obtain deactivation of the impeding means.

4. I have enclosed as Exhibit 1 portions of chapter 10 from the book "Fundamentals of Electrochemical Deposition, entitled "Effect of Additives". The examiner failed to discuss this evidence in support of my theory of how this effect is achieved, and so it is worth reviewing

again.

5. Pages 171-173 describe adsorbate molecular orientation at an electrode surface. On page 172 there is described a change from a parallel or vertical orientation, with just a single constituent bonded to an electrode surface, to an edgewise or horizontal orientation, where the entire molecule is attached or bonded to the electrode surface, which I would consider a film forming orientation, that is, one which coats the entire surface, without the open spaces of the parallel orientation. Changes in adsorbate concentration result in reorientation, the parallel orientation occurring at low concentrations, and there then being an irreversible reorientation to the edgewise configuration occurring as the concentration is increased. Figures 10.5 and 10.6 illustrate the molecular orientation of various molecules, and the packing density for parallel versus edgewise orientation. The parallel or vertical orientation is similar to the type of bonding or attachment of the deactivatable impeding means to the negative electrodes shown in my Figure 6, which is a specific structural arrangement, not related to any method steps as the examiner contends.

6. I have described in the specification how the concentration of the deactivatable impeding means, from as little as 5 mg/l, up to about 1500 mg/l, functions well in accordance with my invention. I had previously presented test results that established that at about a 1 percent concentration of dodecyldimethylbenzylammonium chloride, in a lead acid battery, the impeding means are no longer "deactivatable", that is, do not switch on and off, and remain activated, affecting the discharge cycle, as the cell loses voltage faster, as well as the entire charge cycle, as the cell gains voltage faster. This is proof that there is a reorientation to the edgewise configuration caused by the higher concentration.

7. According to JP50-091728, a concentration of 3% of dodecyldimethylbenzylammonium chloride was added to a Ni-Zn Alkaline battery electrolyte (30% KOH). At such a concentration, in my opinion, deactivatable impeding means are not present, since the orientation would be edgewise, and remain in an activated state during any charging and discharging cycles.

8. To prove this, as well as to distinguish from the '785 patent, I conducted comparative testing to substantially duplicate the conditions of the '728 and 785 patents, as will be discussed below.

9. As to JP10-302785A, it was my opinion that the inclusion of a fatty acid in a paste used to produce an anode could not provide the attachment orientation necessary to provide the claimed deactivatable impeding means. To show that this was indeed the case, comparative testing was performed.

10. I constructed three test cells out of new, unformed lead acid battery plates, by diligently dividing a single positive plate into three identical positive electrodes and a single negative plate into three identical negative electrodes, each cell assembled in a separate glass jar using one of the positive electrodes and one of the negative electrodes and employing sulphuric acid procured from a single source, such that the common sourcing of the electrodes and acid would insure consistency in performance.

11. To one negative electrode, I then used acetone to add the fatty acid (stearic acid) in correspondence to the JP'785 Patent, that is, I dosed the negative electrode with 1 % by weight of stearic acid. Acetone is especially satisfactory, ensuring zero residue. Application in this way most closely approximates the conditions used to produce the JP '785 test cells, and any difference would likely result in conditions more close to my invention, and so would more likely

result in performance closer to my invention. In other words, mixing with the anode paste as described in the Japanese Patent favors complete coating of the electrode surface, because of the uniform mixing, while solvent dosing, while similar, leaves open the possibility that parallel orientation could be achieved.

12. Cells number 2 and 3 were left untreated, and all three cells were connected electrically in series and were charged at 60 mA until formed. Thereafter, all three were discharged down to 1.75 volts per cell and recharged at 60 mA. This ensured that the cells were matched and were capable of providing secondary cell performance.

13. The first measured run was made by discharging all three cells in series at a constant current of 180 mA. Voltage readings of cell 1 and Cell 3, representing the stearic acid treated cell and an untreated cell, were recorded, and the results shown in Graph 2. The cells were allowed to stand in a discharged state for 12 hours and were then recharged in series at a constant current of 60 mA, with voltage readings recorded and the results shown in Graph 1.

14. It is essential to discharge and charge the cells at constant current, so that no matter what the voltage is across the load, the current flowing remains unchanged. The cells, being series connected, then experience identical conditions and meaningful observations can be made. The fact that the current flowing through cell 1 and cell 3 are identical permits a determination on the nature of the effect provided by the stearic acid on the negative electrode of cell 1.

15. It can be seen from graph 1 that the stearic acid provides series resistance, however, contrary to the examiners' contention, the stearic acid effect is always present, and is not activated/deactivated according to the state of charge of the battery, that is, stearic acid does not provide the structure necessary to provide the deactivatable impeding means of my invention.

The effect created, whether by a film or other barrier, remains activated, and is permanent, and so there is no on/off switching effect. The result is that, while providing an increase in the hydrogen overpotential, as evidenced by the rising potential of the stearic acid curve from about 11 hours onward, this also provides a rising potential throughout the bulk of the charging, making the charging process less efficient and causing an increase in ohmic losses in the battery, with an increase in heating. Also, graph 2 shows an increase in resistance during discharging, causing further heating losses and reducing the battery ampere-hour rating, as seen from the curves in graph 2.

16. This test confirms the serious disadvantages inherent in the JP '785 Patent, disadvantages specifically overcome by my invention, by proving that JP '785 Patent does not provide the structure necessary to provide the deactivatable impeding means as required by my claims.

17. Upon completing the stearic acid test, I then undertook to test the use of 3% dodecyl dimethyl benzyl ammonium chloride ("DBAC") in a cell, in correspondence to the JP '728 Patent.

18. Cell 2 was dosed with 3% DBAC, which is highly soluble in sulfuric battery acid. The cells were then left to stand for 24 hours to stabilize the electrolyte of cell 2 following the dosing.

19. Graph 3 shows the charging curves of cell 2 and cell 3 respectively. The DBAC dosed cell initially experienced a more rapid increase in potential, but as cell 3 reached towards its gassing potential, growing progressively faster, the potential of cell 2 flattened. After about 9 hours, cell 2 showed signs of reaching the gassing potential. Charging was stopped when cell 3 had been gassing briskly for about 4 hours, confirming it was fully charged.

20. A serious reduction in performance of cell 2 was evident upon discharging the cells at

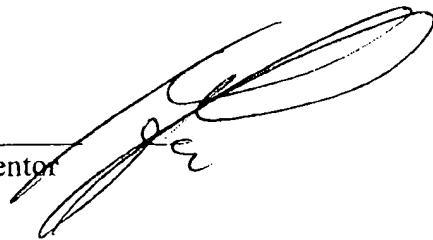
180 mA, constant current, as shown in graph 4, as cell 2 collapsed at 1.25 hours, while cell 3 continued beyond 5 hours.

21. This proves that the JP '728 Patent cell does not have deactivatable impeding means. In the structural sense, which is the examiners' focus, a concentration of 3 % DBAC cannot provide the proper attachment to the electrode necessary to provide the deactivatable impeding means of my invention. The "switch" is simply not there, and it would be wrong to disregard the concentration when looking at the disclosure of this patent. The same structure is not present in the JP '728 Patent, and in fact, one skilled in the art would be quite surprised to learn that there is indeed a structural difference with dramatic improvements in performance related to the type of attachment achieved at different concentrations.

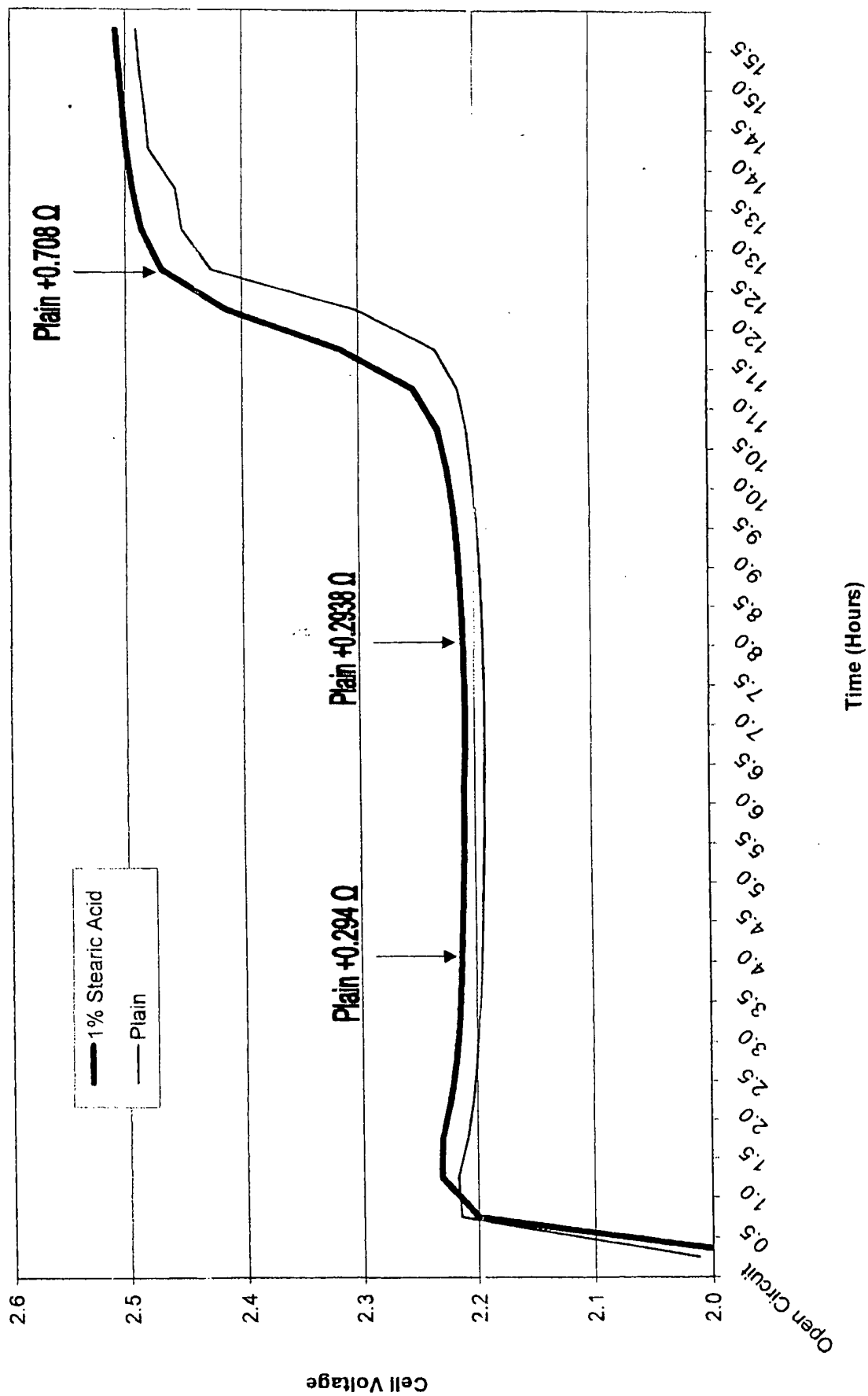
I, the undersigned inventor, further declare that all statements herein of my own knowledge are true and that all statements made on information and belief are believed to be true and further, and that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: DECEMBER 7, 2004

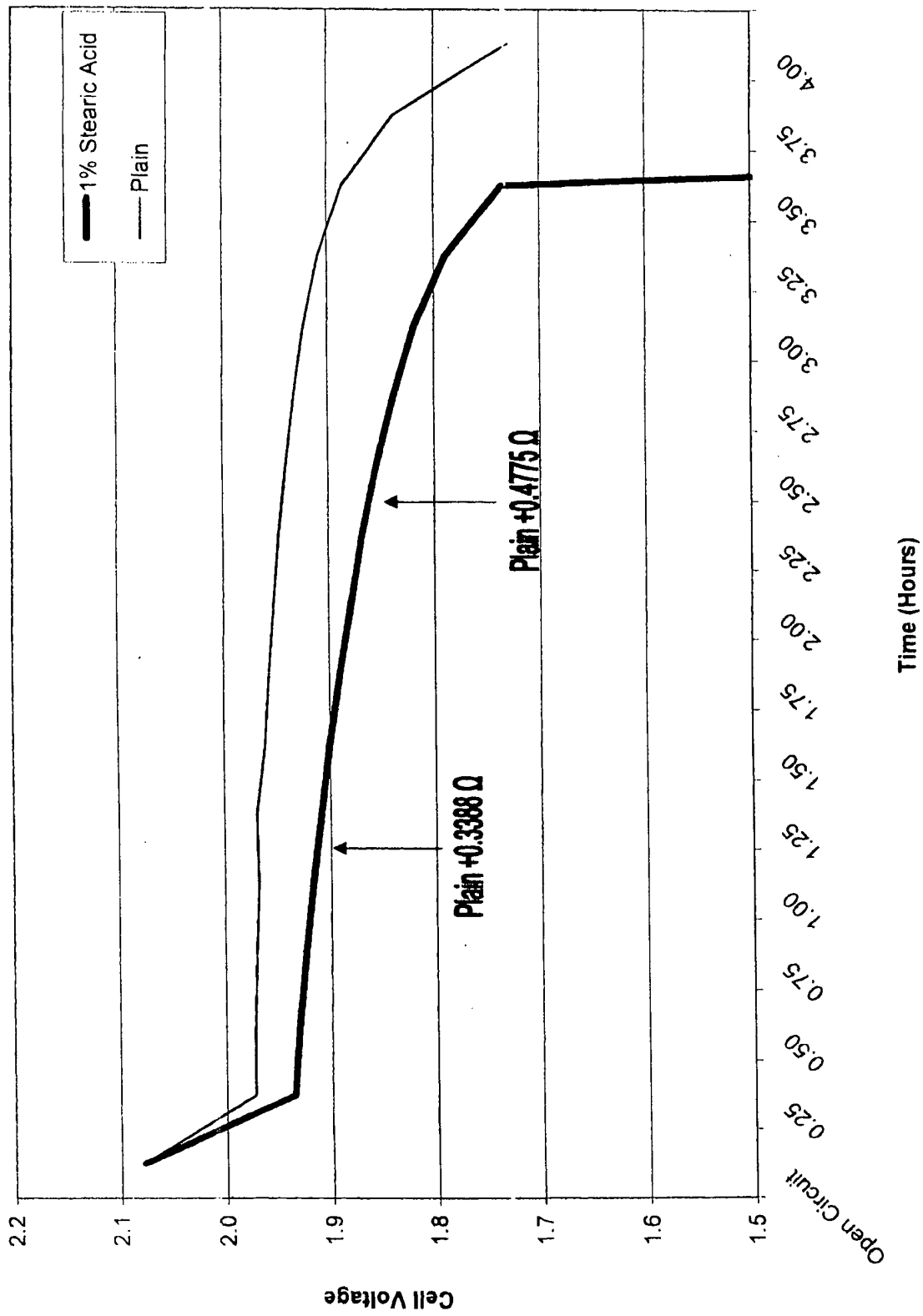
Johan C. Fitter, Inventor

A handwritten signature in black ink, appearing to read 'Johan C. Fitter', is written over a horizontal line. The signature is stylized with a large, sweeping loop at the end.

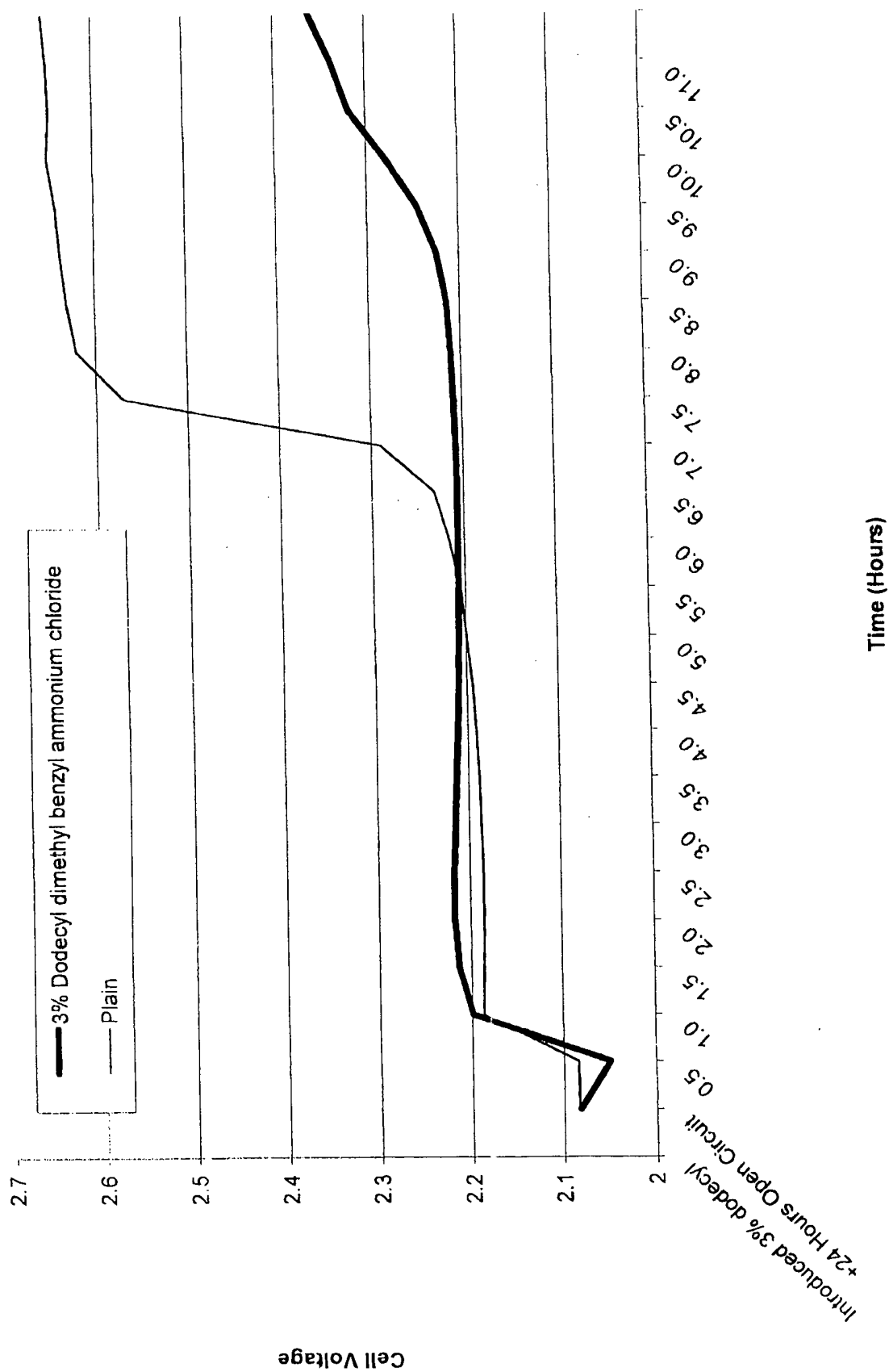
Graph 1 - Charging 0% to 100% at 60 mA



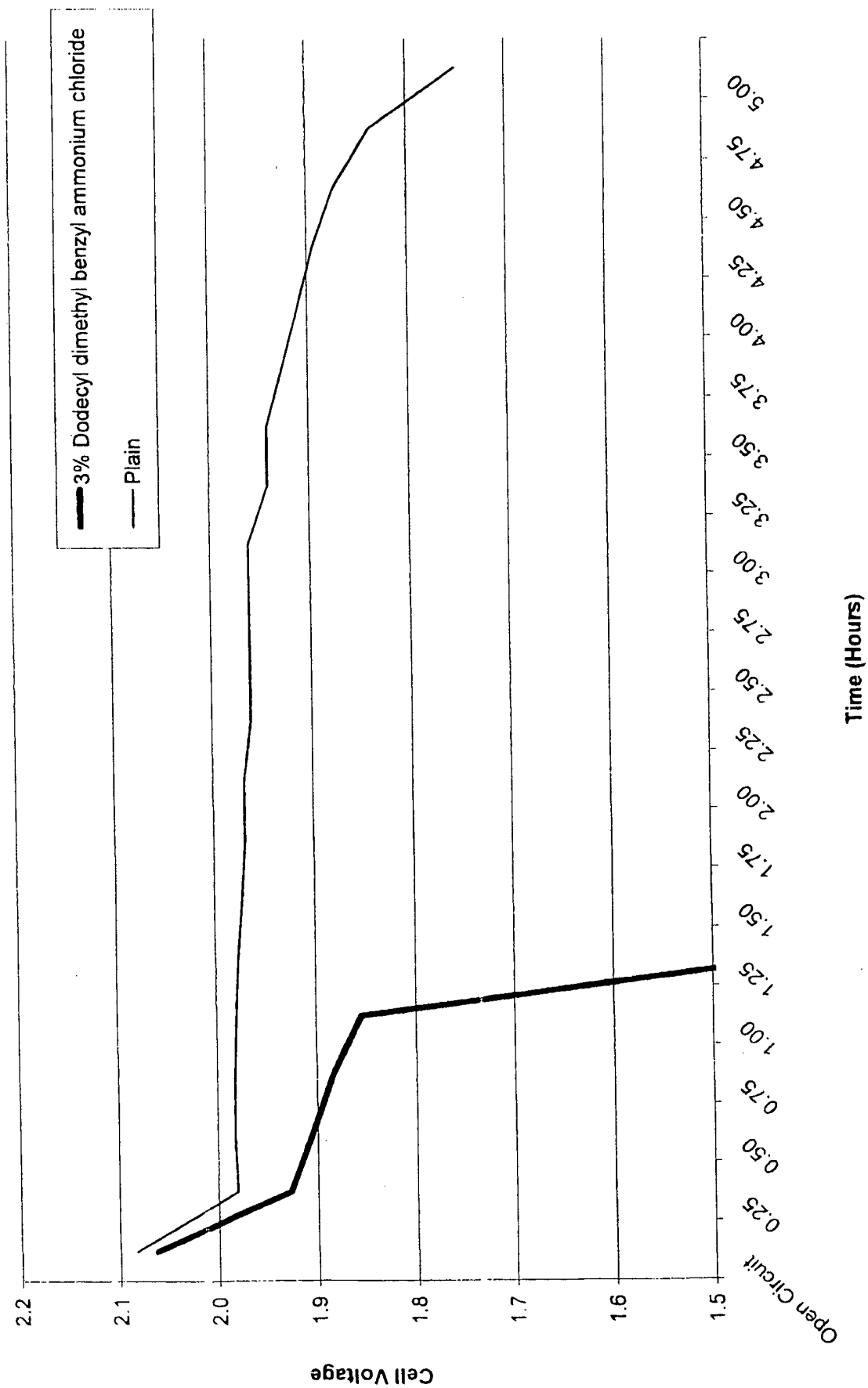
Graph 2 - Discharging 100% to 0% at 180mA



Graph 3 - Charging from about 50% to 100% at 60mA



Graph 4 - Discharging 100% to 0% at 180mA



FUNDAMENTALS OF ELECTROCHEMICAL DEPOSITION

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Reaction (9.14) is a very important displacement deposition reaction in the printed circuit industry. It is used to help the soldering capability of copper.

9.5. KINETICS AND MECHANISM

The kinetics and mechanisms of the displacement deposition of Cu on a Zn substrate in alkaline media was studied by Massee and Piron (5). They determined that at the beginning of the deposition process, the rate is controlled by activation. The activation control mechanism changes to diffusion control when the copper covers enough of the Zn surface to facilitate further deposition of copper. This double mechanism can explain the kinetic behavior of the deposition process.

The mechanisms of the crystal building process of Cu on Fe and Al substrates were studied employing transmission and scanning electron microscopy (1). These studies showed that a nucleation-coalescence growth mechanism (Chapter 7, Section 7.10) holds for the Cu/Fe system and that a displacement deposition of Cu on Fe results in a continuous deposit. A different nucleation-growth model was observed in the case of the Cu/Al system. Displacement deposition of Cu on Al substrate starts with formation of isolated nuclei and clusters of Cu. This mechanism results in the development of dendritic structures.

The properties of deposits may be controlled by changing the kinetics of the deposition and the mechanism of crystallization. One way to achieve this is by complexing the depositing ions, as stated above.

REFERENCES AND FURTHER READING

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3. M. Paunovic and C. H. Ting, in *Electroless Deposition of Metals and Alloys*, M. Paunovic and I. Ohno, eds., PV 88-12, The Electrochemical Society, Pennington, NJ, 1988.
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10

Effect of Additives

10.1. INTRODUCTION

Most solutions used in electrodeposition of metals and alloys contain one or more inorganic or organic additives that have specific functions in the deposition process. These additives affect deposition and crystal building processes as adsorbates at the surface of the cathode. Thus, in this chapter we first describe adsorption and the factors that determine adsorbate-surface interaction. There are two sets of factors that determine adsorption: substrate and adsorbate factors. Substrate factors include electron density, *d*-band location, and the shape of substrate electronic orbitals. Adsorbate factors include electronegativity and the shape of adsorbate orbitals.

After discussing adsorption, we discuss the effects of additives on the kinetic parameters of the deposition process and on the elementary processes of crystal growth.

10.2. ADSORPTION

Chemisorption and Physisorption. One classification of adsorption phenomena is based on the adsorption energy: the energy of the adsorbate-surface interaction. In this classification there are two basic types of adsorption: chemisorption (an abbreviation of *chemical adsorption*) and physisorption (an abbreviation of *physical adsorption*). In chemisorption the chemical attractive forces of adsorption are acting between surface and adsorbate (usually covalent bonds). Thus, there is a chemical combination between the substrate and the adsorbate where electrons are shared and/or transferred. New electronic configurations are formed by this sharing of electrons. In physisorption the physical forces of adsorption, van der Waals or pure electrostatic forces, operate between the surface and the adsorbate; there is no electron transfer and no electron sharing.

Adsorption energy for chemisorbed species is greater than that for physisorbed species. Typical values for chemisorption are in the range of 20–100 kcal/mol and for physisorption, in the range of 5 kcal/mol.

The difference between physisorption and chemisorption can be explained using a potential-energy diagram. The potential-energy diagram for physisorption and chemisorption of an A-A molecule (e.g., H₂) is shown in Figure 10.1. Curve P in

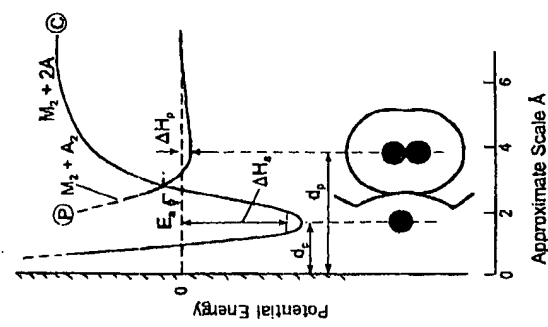


Figure 10.1. The potential-energy diagram for physisorption and chemisorption of an A-A molecule.

Figure 10.1 gives the potential energy of the molecule A_2 for cases in which only physical forces of attraction are operating. It is seen that as the molecule approaches the surface, its energy falls as it becomes physisorbed. The minimum of this curve represents the equilibrium state for the physisorbed molecule. The potential well q_p (ΔH_p), the heat of adsorption for the physisorption, is relatively shallow and is due to long-range forces (e.g., van der Waals forces) so that the equilibrium distance from the surface (d_p) is relatively large. It is located at the sum of the van der Waals radii for the surface atom and the adsorbate A_2 molecule. An attempt to decrease the distance of separation below the equilibrium value leads to gradually increasing repulsion. Curve C corresponds to the interaction of two A atoms with the surface. The minimum of this curve represents the equilibrium state for chemisorbed atoms A. The minimum is deeper and at a smaller distance (d_c) than the one for physisorption (d_p). The two curves (P and C, Fig. 10.1) cross, and the adsorbate can pass from the first to the second. The transition from physisorption to chemisorption occurs at the crossing point of curves P and C. The energy at this point is the activation energy E_a , which is the excess of energy of that for the separated metal and A_2 molecule. It is the activation energy for the transition from physical to chemical adsorption. Figure 10.1 shows that chemisorption in this case involves dissociation of physisorbed molecules.

Adsorption Equilibrium. Since the additive is not used up in many cases of electrodeposition in the presence of an additive (the additive is not incorporated in the deposit), one can conclude that the adsorption equilibrium is dynamic. In a dynamic adsorption equilibrium state the adsorbed molecules are continually desorbing at a rate equal to the rate at which dissolved molecules from the solution

become adsorbed. If the rates of the adsorption and desorption processes are high and of the same order of magnitude as that of the cathodic deposition process, then no incorporation, or entrapment, of additives in the deposit will occur. However, if they are much smaller, additive molecules will be entrapped in the deposit via propagating steps (growing crystallites). Thus, at a current density higher than the optimum value, additives (brighteners or levelers) will be incorporated into the deposit. This incorporation can result in poor quality of the resulting deposit.

Adsorption Isotherms. Adsorption isotherms describe the relationship between the coverage θ of the surface by the adsorbate and the concentration of the adsorbate in the bulk solution, c^b , at a given temperature. The surface coverage θ is defined as

$$\theta = \frac{N_{\text{occ}}}{N} \quad (10.1)$$

where N_{occ} and N are the number of adsorption sites occupied and the total number of adsorption sites available, respectively. From this equation it follows that $N\theta = N_{\text{occ}} =$ number of adsorption sites occupied, and $N - N_{\text{occ}} = N - N\theta = N(1 - \theta) =$ number of vacant sites.

The relationship $\theta = f(c^b)$ can be derived from a kinetic model assuming that the rate of adsorption r_a is proportional to the number of vacant sites $N(1 - \theta)$ and also to the bulk solution concentration c^b

$$r_a = k_a N(1 - \theta) c^b \quad (10.2)$$

and that the rate of desorption r_d is proportional to the number of adsorption sites occupied, $N\theta$

$$r_d = k_d N\theta \quad (10.3)$$

where k_a and k_d are adsorption and desorption rate constraints, respectively. At dynamic equilibrium $r_a = r_d$ and

$$k_a N(1 - \theta) c^b = k_d N\theta \quad (10.4)$$

Solving for θ , one obtains the Langmuir isotherm (Section 10.3, Ref.1)

$$\theta = \frac{Kc^b}{(1 + Kc^b)} \quad (10.5)$$

where $K = k_a/k_d$ is the adsorption equilibrium constant.

The Langmuir isotherm is based on the simplest model that involves the following assumption: (1) the adsorption energy of all sites is the same and is unaffected by adsorption on neighboring sites, (2) the adsorption is immobile, (3) each site accommodates only one adsorbed particle, and (4) adsorbed atoms (molecules) do not interact with each other. Figure 10.2a shows that the Langmuir-type isotherm for

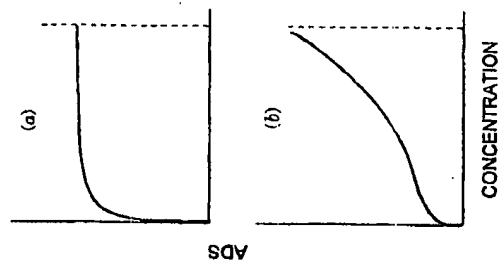


Figure 10.2. Types of adsorption isotherms: (a) Langmuir type; (b) physisorption, multilayer.

chemisorption has a limiting adsorption that corresponds to a monolayer coverage. In contrast, isotherm for a physisorption (Fig. 10.2b) does not show a saturation plateau but indicates a multilayer formation.

Equation (10.5) is valid for cases where there is no dissociation on adsorption. However, in many cases chemisorption is dissociative, involving, for example, adsorption of hydrogen (H_2). In these cases the chemisorption process can be formulated as shown in Figure 10.3. If the adsorbed molecule dissociates into n fragments, then the Langmuir isotherm has the form

$$\theta = \frac{K(c^b)^{1/n}}{1 + K(c^b)^{1/n}} \quad (10.6)$$

If a molecule is being adsorbed on m sites on the surface, without dissociation, the following equation holds:

$$\frac{\theta}{(1 - \theta)^m} = Kc^b \quad (10.7)$$

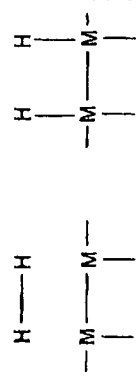


Figure 10.3. Dissociative adsorption of H_2 molecule.

Adsorption isotherms for n -decylamine on Ni, Fe, Cu, Pb, and Pt at the potential of maximum adsorption are shown in Figure 10.4. It is seen that a limiting coverage is approached in each case except on Pt, where multilayer formation occurs. The coverage θ in this case is defined as

$$\theta = \frac{\Gamma}{\Gamma_s} \quad (10.8)$$

where Γ is the surface concentration of adsorbate (mol/cm^2) and Γ_s is the saturation coverage of electrode by adsorbate (or Γ_{max}). In this case Γ_s is $7.9 \times 10^{-10} \text{ mol}/\text{cm}^2$ (Γ_s in Fig. 10.4). Thus, a very small amount of material is involved in adsorption. This case is of interest since this small amount of adsorbent can influence the type of deposit, as is shown in Section 10.5.

Simultaneous Adsorption of Two or More Species. If there are N different additives adsorbed at the electrode, the total surface coverage θ_T is given by

$$\theta_T = \theta_1 + \theta_2 + \theta_3 + \dots + \theta_N \quad (10.9)$$

where $\theta_1, \theta_2, \theta_3, \dots, \theta_N$ is the surface coverage of additive $A_1, A_2, A_3, \dots, A_N$, respectively.

Adsorbate Molecular Orientation at Electrode Surface. Adsorption of some molecules from solution produces an oriented adsorbed layer. For example, nicotinic acid (NA, or 3-pyridinecarboxylic acid, "niacin" or vitamin B_3) is attached to a Pt(111) surface primarily or even exclusively through the N atom with the ring in a (nearly) vertical orientation (Section 10.3, Ref. 12) (Fig. 10.5a).

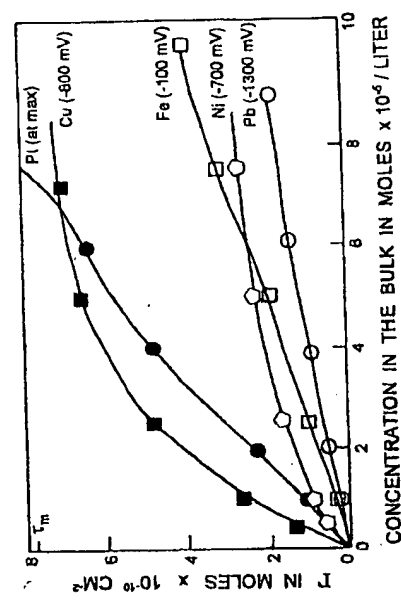


Figure 10.4. Adsorption isotherms for n -decylamine on Ni, Fe, Cu, Pb, and Pt at the potential of maximum adsorption. (From Ref. 5 in Section 10.3, with permission from the Electrochemical Society.)

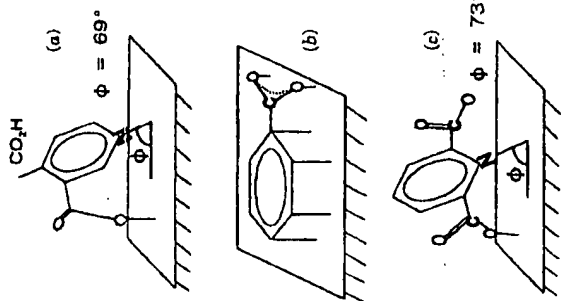


Figure 10.5. Adsorbate molecular orientation at the electrode surface: (a) benzoic acid; (b) benzoic acid; (c) 2,6-pyridinedicarboxylic acid. (From Ref. 12 in Section 10.3, with permission from the American Chemical Society.)

In another example, benzoic acid (BA) is an aromatic compound that orients horizontally at a Pt(111) surface (Fig. 10.5b). This horizontal orientation of adsorbed BA involves coordination of the carboxylic acid to the Pt surface. The coordination depends on surface potential (Section 10.3, Ref. 12). BA adsorbed at negative potentials is coordinated to the Pt through the aromatic ring and (primarily) one carboxylate oxygen; when adsorbed at positive potentials, it is coordinated to the Pt surface through two equivalent oxygens. 2,6-Pyridinedicarboxylic acid (2,6 PDA) adsorbs in a tilted fashion with $\theta = 73^\circ$, as seen in Figure 10.5c. When adsorbed at negative potentials, it is coordinated by one, not both, carboxylates to the Pt surface; in contrast, when adsorbed at positive electrode potentials, it is coordinated by both carboxylates to Pt, each through one oxygen.

Change in adsorbate concentration in solution can also result in orientational changes of molecules on the surface. For example, Soriaga et al. (Section 10.3, Ref. 10) have shown that diphenols and quinones are adsorbed on Pt electrodes with the diphenol or quinonoid ring parallel to the substrate at low concentration and reorient irreversibly to edgewise orientations as the concentration is increased. Figure 10.6 illustrates the way the average area occupied by a single molecule in the adsorbed layer depends on the orientation of the adsorbate on the surface, and how the molecular packing density, expressed in mol/cm², depends on adsorbate molecular orientation. Thus, the adsorbate orientation and orientational transitions are of fundamental and practical interest because of their influence on the kinetics and mechanism of electrochemical deposition.

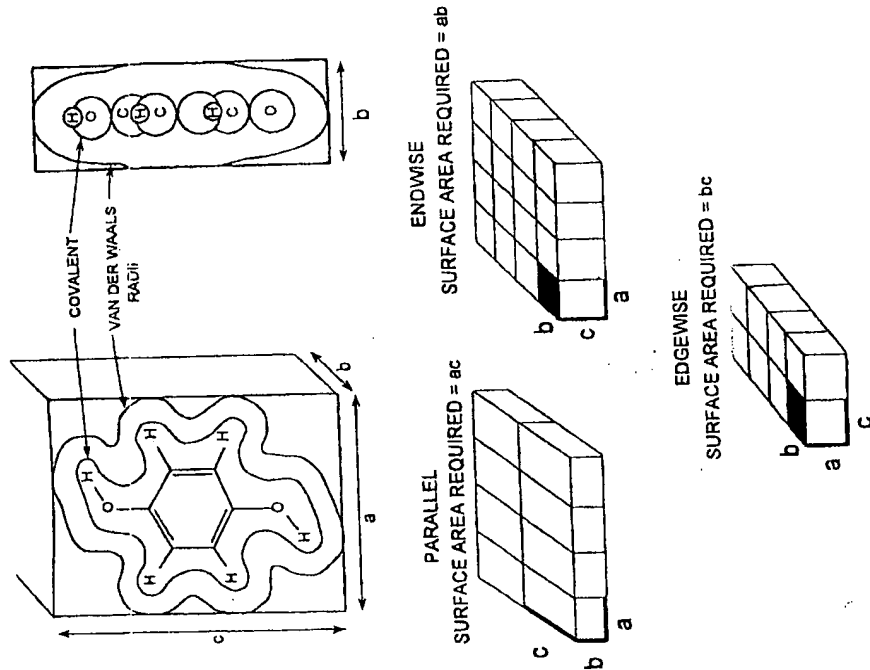


Figure 10.6. The orientation of adsorbate on the surface and the molecular packing density. (From Ref. 10 in Section 10.3, with permission from Elsevier.)

Adsorption of Polymers. The three major characteristics of polymers in the metal-solution interphase, of interest in metal deposition, are polydispersity, large number of configurations, and number of points of attachments. Polymers used as additives (e.g., wetting agents) as prepared are generally polydisperse. Their adsorption has to be treated as a multicomponent system. For good reproducibility in metal deposition, it is important to use relatively limited-molecular-weight fractions. A large number of configurations and the number of points of attachment are factors that determine the rate of attainment of adsorption equilibrium.

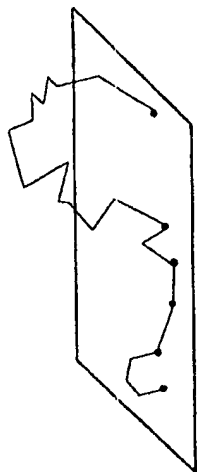


Figure 10.7. Schematic representation of adsorbed polymer.

The shape of flexible polymer molecule in the vicinity of the surface is greatly distorted from the average shape in solution. Adsorbed polymer molecules are attached to the surface by stretches of segments at the surface alternating with loops out of the surface (Fig. 10.7).

10.3. EXPERIMENTAL METHODS FOR STUDY OF ADSORPTION

Potentiodynamic Technique. Adsorption of methanol on Pt in acid solution was studied by Breiter and Gilman (3) using potentiostatic technique. The anodic sweep, with a sweep rate of 800 V/s, was started at rest potential and extended to 2.0 V, with respect to hydrogen reference electrode in the same solution. As shown in Figure 10.8, the current was recorded as a function of potential (time) in the absence (curve A) and in the presence (curve B) of methanol. The increase in the current in curve B is due to oxidation of the adsorbed methanol on the platinum electrode. Thus, the shaded area 2 minus the shaded area 1 (Fig. 10.8) yields the change Q_M (C/cm^2) required for the oxidation of the adsorbed methanol:

$$Q_M = \int_0^t i_B dt - \int_0^t i_A dt \quad (10.10)$$

The applicability of this technique is based on four assumptions: (1) the number of coulombs per square centimeter used for the anodic formation of an oxygen layer ($2OH^- = O_{ads} + H_2O + 2e$) and the oxygen evolution during the sweep is the same in either the absence or presence of methanol; (2) the same number of electrons per molecule, independent of the amount of the adsorbed methanol, is used up in the oxidation; (3) the double-layer charging current is the same in the presence or absence of methanol; and (4) the anodic sweep is sufficiently fast (here 800 V/s) such that oxidation of methanol, which diffuses from the bulk solution to the electrode during the sweep, is negligible (i.e., only the adsorbed methanol is oxidized).

Galvanostatic Transient Technique. Breiter (4) measured the adsorption of formic acid (HCOOH) on platinum in the solution of perchloric acid (HClO₄) using

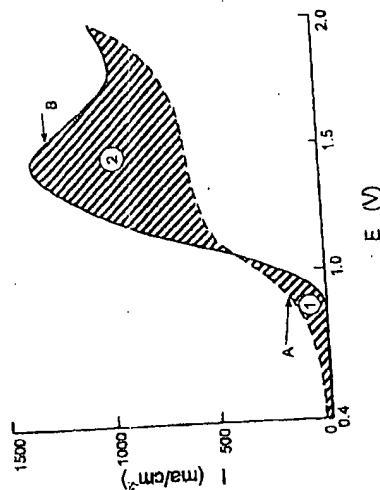


Figure 10.8. Potentiostatic i - E curves with $V = 800$ V/s in HClO₄ + 1 M CH₃OH (curve B) and in 1 N HClO₄ (curve A) starting from the open-circuit potential. (From Ref. 3, with permission from the Electrochemical Society.)

galvanostatic transient technique. Figure 10.9 shows two anodic galvanostatic transients at 91 mA/cm² on Pt in HClO₄ (curve a) and in HClO₄ + HCOOH (curve b). Curve a corresponds to the anodic formation of an oxygen layer (Pt-O) on Pt. The completion of about a monolayer Pt-O is reached at the transition time τ_0 (after the completion of about a monolayer Pt-O corresponds to a simultaneous oxidation of adsorbed HCOOH molecules and the formation of the adsorbed HCOOH. The plateau at about 1.0 V results from the oxidation of the adsorbed HCOOH (formic acid) transition time τ_F for the oxidation of the adsorbed HCOOH (formic acid) molecules alone is

$$\tau_F = \tau - \tau_0 \quad (10.11)$$

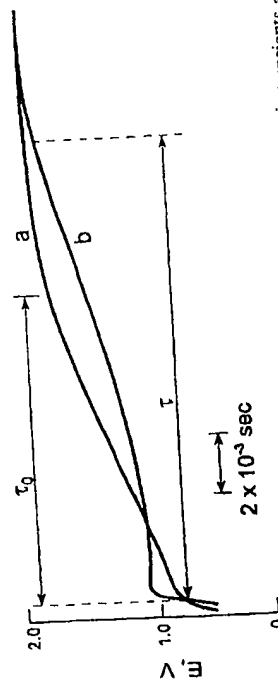


Figure 10.9. Anodic charging curves from 0.4 V during the galvanostatic transients anodic potential sweep at 91 mA/cm² in 1 N HClO₄ (curve a) and in 1 N HClO₄ + HCOOH (curve b). (From Ref. 3, with permission from the Electrochemical Society.)

This equation is written assuming that (1) the charging of the double layer requires approximately the same charge Q [number of coulombs per square centimeter (Coul/cm²)] for curves a and b , (2) the number of coulombs per square centimeter for the anodic formation of an oxygen layer on Pt is the same for curves a and b ; and (3) oxidation of HCOOH molecules that diffuse to the Pt electrode is negligible since the transition times are short enough (order of 10⁻³ sec). The coverage θ_F of formic acid molecules is given as

$$\theta_F = \frac{\tau_F}{\tau_{F,m}} = \frac{\tau - \tau_0}{\tau_m - \tau_0} \quad (10.12)$$

where $\tau_{F,m}$ refers to a monolayer of HCOOH molecules (or, τ_m is the limiting value of τ_F).

Chronopotentiometry. Pounovic and Oechsli (8) measured the adsorption of peptone on lead-tin alloy electrodes using chronopotentiometric and double-layer measurements. This case is different from the previous (adsorption of HCOOH) since peptone is not an electroactive species in the studied conditions, but it only blocks the surface used for the electrodeposition of lead-tin alloys from the solutions containing Sn²⁺ and Pb²⁺ ions. Chronopotentiometric analysis is based on the following principles (7). In the absence of adsorption, the relationship between the transition time τ (for reduction of Sn²⁺ and Pb²⁺ in this case), the bulk concentration c^0 of the substance reacting at the electrode, and the current I is given by the equation

$$\sqrt{\tau} = \frac{nFA\sqrt{\pi D}}{2I} \quad (10.13)$$

where n is the number of electrons involved in the reaction, F is the Faraday constant, A is the surface area of the electrode, and D is the diffusion coefficient (diffusivity). For a given system and for a constant current, Eq. (10.13) reduces to

$$\sqrt{\tau} = kAc^0 \quad (10.14)$$

where the constant $k = (nF\sqrt{\pi D})/2I$. In the presence of adsorption, the adsorbed substances that are neither reduced nor oxidized at the electrode block a part of the electrode surface and the result of this blocking is a decrease in available surface area for the electrode reaction (here the deposition of Pb and Sn).

Thus, the surface area A in Eqs. (10.13) and (10.14) must be replaced by the available (free, unoccupied) surface area. This surface area, which is free for the electrode reaction, can be expressed in terms of the surface coverage θ . The fractional surface coverage θ of the electrode surface by an adsorbed substance is defined as

$$\theta = \frac{A_1}{A} \quad (10.15)$$

where A is the total surface area and A_1 the occupied surface area of the electrode. From Eq. (10.15) it follows that the unoccupied surface area A_2 is

$$A_2 = A - A_1 = A(1 - \theta) \quad (10.16)$$

since, from Eq. (10.15), $A_1 = \theta A$.

Finally, the chronopotentiometric equation, for a given system and for constant current, in the presence of adsorption is obtained by substituting A in Eq. (10.14) with A_2 from Eq. (10.16), thus

$$\sqrt{\tau} = kA_2c^0 = kA(1 - \theta)c^0 \quad (10.17)$$

It is seen from Eq. (10.17) that an increase in θ causes a decrease in the transition time τ . If τ_0 is the transition time in the absence, and τ in the presence of adsorption of the electrochemically inactive additives, then the difference

$$\Delta\tau = \tau_0 - \tau \quad (10.18)$$

is a function of the amount of the adsorbed additive. Typical chronopotentiograms for the reduction of Sn²⁺ and Pb²⁺ in both absence and presence of peptone are

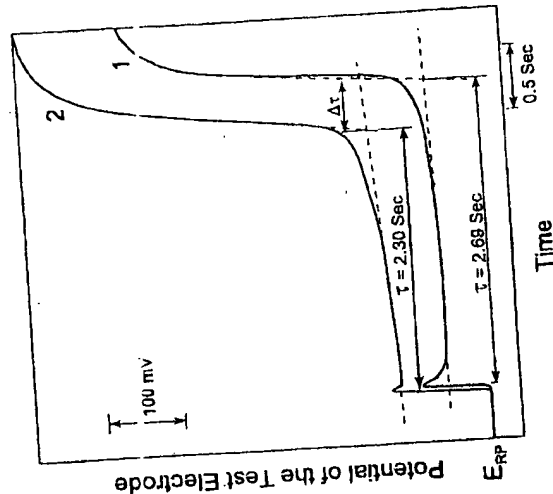


Figure 10.10. Change of transition time for reduction of Pb²⁺ and Sn²⁺ due to adsorption of peptone: 1—chronopotentiogram in the absence of peptone; 2—Chronopotentiogram in the presence of 4 g/L peptone; E_{RP} —the rest potential. (From Ref. 8, with permission from the American Electroplaters and Surface Finishers Society.)

shown in Figure 10.10. At the transition time τ all the available Sn^{2+} and Pb^{2+} ions at the electrode surface are reduced and a new process starts (evolution of hydrogen). The difference $\Delta\tau$ is a function of the bulk concentration of the additive and increases with increasing concentration of the additive according to an adsorption isotherm. Thus, measurements of $\Delta\tau$ can be used to determine concentration or adsorption properties of additives in a solution.

The fractional surface coverage θ can be calculated from the experimental values of τ_0 , τ , and τ_m using the equation

$$\theta = \frac{\tau_0 - \tau}{\tau_0 - \tau_m} \quad (10.19)$$

where τ_m is the transition time for the limiting (saturation) value of adsorption.

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10.4. EFFECT OF ADDITIVES ON KINETICS AND MECHANISM OF ELECTRODEPOSITION

In the discussion of atomistic aspects of electrodeposition of metals in Chapter 6 (Section 6.8), it was shown that in electrodeposition the transfer of a metal ion M^{n+} from the solution into the ionic metal lattice in the electrodeposition process may proceed via one of two mechanisms: (1) direct mechanism in which ion transfer takes place on a kink site of step edge or on any site on the step edge (any growth site) or (2) terrace site ion mechanism. In the terrace site transfer mechanism a metal ion is transferred from the solution (OHP) to the flat face of the terrace region. At this position the metal ion is in adion state and is weakly bound to the crystal lattice. From this position it diffuses on the surface seeking a position with lower potential energy. The final position is a kink site.

Adsorbed additives affect both of these mechanisms by changing the concentration of growth sites c_{gs} on the surface [n_g/cm^2 , (where n_g is the number of growth sites)], concentration of adions, c_{ad} , on the surface, diffusion coefficient D_{ad} , and the activation energy E_{ad} of surface diffusion of adions.

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10.5. EFFECT OF ADDITIVES ON NUCLEATION AND GROWTH

In Chapter 7 different growth models were described: layer growth (Section 7.9), nucleation-coalescence growth (Section 7.10), development of texture (Section 7.11), columnar microstructure (Section 7.12), and other structural forms (Section 7.13). In this section we discuss the effect of additives on these growth mechanisms.

Nucleation. In the presence of adsorbed additives the mean free path for lateral diffusion of adions is shortened, which is equivalent to a decrease in the diffusion coefficient D (diffusivity) of adions. This decrease in D can result in an increase in adion concentration at steady state and thus an increase in the frequency of the two-dimensional nucleation between diffusing adions.

Layer Growth. In Chapter 7 (Section 7.9) we showed that many monoatomic steps can unite (bunch, coalesce) to form polyatomic steps in the presence of impurities. Additives can also influence the propagation of microsteps and cause bunching and formation of macrosteps.

Dependence of Types of Deposit on the Surface Coverage by Additive. Type of deposit obtained at constant current density may depend on the value of the surface coverage θ by an additive. Damjanovic et al. (2) studied the effect of various values of the surface coverage θ of n -decylamine on the growth form of copper on the (100) plane of copper single crystal at 5 mA/cm². The surface coverage θ was varied by addition of a known amount of n -decylamine to a highly purified solution of CuSO_4 , H_2SO_4 , and H_2O . The coverage θ of n -decylamine was estimated from the adsorption isotherm for n -decylamine on copper in 1 N NaClO_4 (Fig. 10.4).

It was found that when $\theta < 10^{-2}$ (at the bulk concentration of n -decylamine

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